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OPTICALLY TRANSPARENT GLASS CERAMICS WITH A LOW TEMPERATURE EXPANSION COEFFICIENT

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Principles for producing optically transparent glass ceramics from industrial waste are considered. The intensity of their transmission spectra in the visible spectrum range and the temperature dependence of the logarithm of volume resistivity, thermal conductivity, and TCE are considered. It is demonstrated that adding 30% lithium oxide to the glass-ceramic composition decreases its TCE.

Optically transparent glass ceramics find wide application in the construction industry. They were first obtained on the basis of spodumene glasses made from pure oxide materials, as well as some other compositions of the systems $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$, $\text{Li}_2\text{O} - \text{Ga}_2\text{O}_3 - \text{SiO}_2$, $\text{K}_2\text{O} - \text{TiO}_2 - \text{SiO}_2$, etc. [1]. Numerous studies dedicated to production of glass ceramics based on industrial waste (RF Patent No. 2052400) [2–7] listing these compositions give practical recommendations with respect to glass-melting temperatures and crystallization conditions for glass ceramics; however, they do not address purification of recycling waste from iron and other transitional metal impurities, whose presence in a batch imparts dark colors to glass ceramics and restricts their application areas. The process of extracting low concentrations of iron from waste is not yet sufficiently investigated.

Accordingly, the purpose of our study was to obtain material with a stable chemical composition purified from iron oxides and impurities of transition metals for the production of optically transparent glass ceramics with a low temperature coefficient of expansion (TCE).

Direct reduction of iron oxide is implemented as follows. Before heating a batch with a known chemical composition, the carbon content in it is brought to 3–8% (here and elsewhere mass content) depending on the iron oxide content. The prepared batch is melted in a graphite crucible, then the melt with a total iron content of 0.05–0.10% is chilled under a thermal shock by casting in water (RF Patents Nos. 2052400, 2114797, and 2146234). As the result, an amorphous porous white-colored material of a stabilized composition is obtained. The porous material (foam silicate) consists of solid highly porous swelled granules of fractions 0.1–40.0 mm. Its chemical composition is (%): 45.00 SiO_2 ,

10.00 Al_2O_3 , 0.11 Fe_2O_3 , 37.00 CaO , 7.20 MgO , 0.28 Na_2O , 0.35 K_2O , and 0.11 SO_3 . The material is used as a sound-proof and heat-insulating filler in civil engineering and also as initial material for the production of glass ceramics, transparent in the visible spectrum range [8, 9].

The foam silicate obtained was melted in an alundum crucible at a temperature of 1723 K for 2 h, then poured into a mold preheated to 823 K and subjected to devitrification for 6 h according to a particular schedule. Samples for studying were cast out in the shape of washers of diameter 16 mm and height 1 mm. The end surfaces were polished to achieve a surface finish of class 14. The transmission spectra were recorded using a Spekord spectrophotometer in a wavelength range from 30×10^3 to $14 \times 10^3 \text{ cm}^{-1}$, which corresponds to the visible spectrum range, including parts of ultraviolet and short-range infrared radiation.

The chemical analysis of samples was carried out according to the standard methods (GOST 5382–73). The TCE was measured on an optical-mechanical dilatometer with a low-temperature extension and thermal conductivity was measured on a IT λ -400 set. The measurements were performed in a temperature interval of 180–700 K. Diffraction patterns were registered on a DRON-3 diffractometer using CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$) in an interval 2θ from 5 to 70° . The temperature dependence of volume resistivity was determined by the bridge method and viscosity was measured using a vibration viscometer. Dielectric loss and the dielectric constant were measured under a frequency of 1 MHz. Microhardness was determined on a PMT-3 microhardness meter by indentation of a diamond pyramid, and the compression and bending strength on a test breaking machine IR 5047-50-03.

It can be seen in Fig. 1 that the edge of the transmission band of the sample is within the frequency range of $30 \times 10^3 \text{ cm}^{-1}$. The intensity of transmission spectrum is

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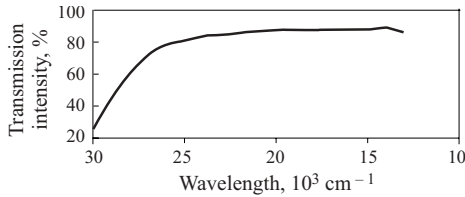


Fig. 1. Intensity of transmission spectra of transparent glass ceramics.

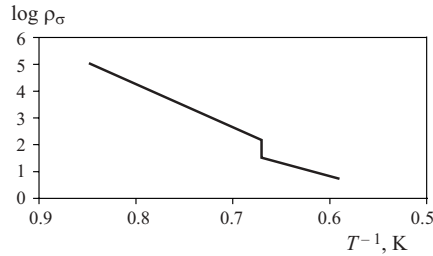


Fig. 2. Dependence of specific volume resistance on temperature.

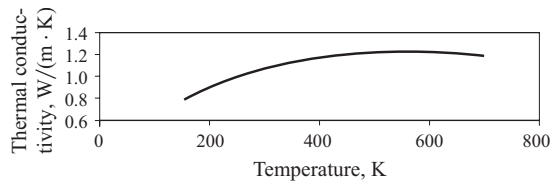


Fig. 3. Temperature dependence of thermal conductivity of material obtained.

85% in the range of $23 \times 10^3 \text{ cm}^{-1}$; it increases, reaching a maximum value of 90% in the interval of $14 \times 10^3 \text{ cm}^{-1}$, and then gradually decreases as the wavelength increases, in the IR range. Based on the transmission spectra specifics, it is positive that these glass materials can be successfully used as a basis for band filters in the visible and short-IR spectrum ranges, as well as substrates for polycrystalline films of ferrogarnets used as magneto-optic information carriers [10].

The electric conductance of glasses and glass ceramics is predominantly ionic, which is related to the presence of mobile alkali cations (Na, K, Ca), which determines the conductivity level depending both on the type of ion and on its concentration. As temperature increases, the conductivity of glass materials grows and resistivity decreases.

A sharp change in volume resistivity is registered within the reverse temperature range (0.67 K^{-1}), which is evidence of structural modifications in the melt (Fig. 2). The conductance activation energy (calculated based on the curve angle) in the range of reverse temperatures $0.59 - 0.67 \text{ K}^{-1}$ is 1.8 eV, and in the range of $0.67 - 0.81 \text{ K}^{-1}$ it is 3.34 eV. The increase in the conductance activation energy is related to growth of the energy barrier that migrating ions have to overcome. The change in the barrier value can be due to the for-

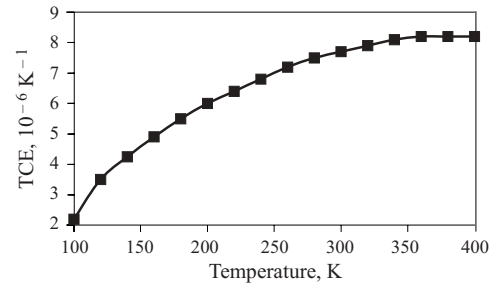


Fig. 4. TCE versus temperature.

mation of crystallization seeds and to changes in the degree of ionicity and covalence of the charge carriers in the melt. It should be noted as well that ionic conductance is related to the dielectric loss tangent, whose numerical value for the particular material is 0.007. The dielectric constant is equal to 14.5.

Mechanical properties of glass ceramics obtained

Strength, MPa:

compressive 600

bending 90

Microhardness, MPa 8500

The thermal conductivity of the material monotonically grows with increasing temperature to a value of $1.23 \text{ W/(m} \cdot \text{K)}$ and decreases significantly with further increase in temperature (Fig. 3). Such behavior of the temperature dependence of thermal conductivity is evidently typical only of glass ceramics, since the thermal conductivity of glasses uniquely grows with increasing temperature, and in crystalline materials it uniquely decreases [11].

The advantage of the proposed method for producing optically transparent glass ceramics from industrial waste consists in the possibility of crystallization of amorphous phases with different values and even different signs of the TCE. A typical example of the temperature dependence of the TCE of clear glass ceramics is shown in Fig. 4.

It can be seen that the TCE in the low-temperature range is equal to $2.5 \times 10^{-6} \text{ K}^{-1}$; as temperature increases, the TCE monotonically grows, reaching a value of $7.7 \times 10^{-6} \text{ K}^{-1}$ at room temperature (300 K). On further temperature increase up to 350 K the rate of change of the TCE decreases and after reaching a temperature of 360 K up to 390 K it remains constant and equal to $8.2 \times 10^{-6} \text{ K}^{-1}$.

The following polynomial was chosen for approximation of experimental results:

$$\alpha = A + BT + CT^2 + DT^3 + ET^4,$$

where $A = -6.707219$; $B = 0.144901$; $C = -6.644494 \times 10^{-4}$; $D = 1.579611 \times 10^{-6}$; $E = -1.477834 \times 10^{-9}$.

The calculated TCE values are virtually no different from experimental data. Since the TCE depends on the

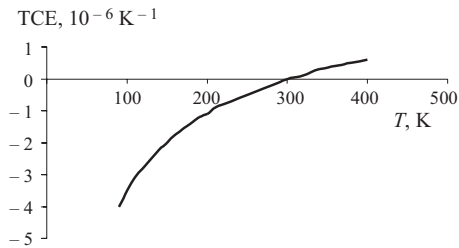


Fig. 5. Temperature dependence of TCE of a sample with lithium additive.

chemical composition of glass ceramics and the quantitative ratio between the crystallizing phases and the residual vitreous phase, it becomes possible to obtain glass ceramics with low TCE values. By adding lithium oxide into a batch, it is possible to obtain a glass ceramic material with zero TCE, which is a result of summing up coefficients with equal modulus and opposite signs. Figure 5 shows the temperature dependence of TCE of a glass-ceramic material containing 30% lithium oxide.

It can be seen that the TCE in the low-temperature range has a negative value, which decreases to zero, as temperature grows to 300 K, then changes its sign and with temperature growing to 400 K becomes equal to $0.6 \times 10^{-6} \text{ K}^{-1}$, which approaches the TCE value of α -quartz. The diffraction pattern of the material obtained has the phase of eucryptite, which has a negative value of TCE [1]. Adding lithium oxide to the batch not only decreases the TCE, but also alters its sign in the low-temperature range.

Thus, using the reducing melting method, it is possible to obtain materials with a stabilized chemical composition in an

x-ray-amorphous state for the production of glass ceramics transparent in the visible spectrum range, whose properties are not inferior to those of optically transparent glass ceramics made of pure oxide materials.

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